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THE RELATION OF SOME OF THE RARER ELEMENTS IN SOILS AND PLANTS.

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INTRODUCTION.

In an earlier publication[1] there were given the results of the examination of a number of important American soil types for the presence of certain of the rarer elements for which reliable methods of analysis had been developed and which it seemed likely might occur in soils.

When this work was completed, it seemed desirable to know whether the rare elements found in soils occurred in plants grown on these soils. If a certain element, though present in minute amounts only, is absorbed by a particular species of plant in relatively large quantities and occurs in other plants in traces only, it would seem reasonable to assume that the element in question has some physiological function. In such cases the element must be in the soil in sufficient quantity or added in the form of fertilizer. There is but little in the literature of plant physiology pertaining to the physiological action of the rarer elements in plant tissues. Frequently when culture experiments have been carried on the elements tested have been found toxic.

Some of the rarer elements very much resemble the commoner ones in chemical reaction. Notable examples are the resemblances of vanadium and phosphorus and of rubidium and potassium.

[1] Bul. 122, U. S. Dept. of Agriculture (1914).

11192°—17—Bull. 600——1

In Wolff's tables, which are the only comprehensive compilation of ash analyses, iron and aluminum are seldom differentiated, and the data given for sulphur are known to be too low.[1] For the matter under consideration in this paper these tables are of no value, for rarer elements were not considered.

In the present work the number of elements sought for has been limited by the lack of accurate methods and the improbability of finding certain elements. Titanium, vanadium, chromium, molybdenum, barium, strontium, lithium, rubidium, and caesium have been determined.

Partly for the sake of completeness, and partly because the authors wished to find out if there has been a replacement by a less common but similar element, the commoner elements have also been determined. The data obtained are by no means complete. The variation of the composition of varieties was ignored; the variation of the plant at different periods of growth and the variation in the composition of plants grown on different types of soil are only meagerly covered.

The presence of some of the rarer elements in plants has been previously reported. The references given below include only those elements for which the plants used in this work were examined.

BARIUM.

Hornberger[2] found 0.97 and 1.20 per cent BaO in two samples of ash from the trunks of copper beeches. He reports the results of earlier investigation in which the presence of barium in beech, oak, birch, and wheat is noted. Crawford[3] supposes the poisonous action of loco weed to be due to barium compounds. There is a comparatively large amount of barium present (0.021 BaO in the dried plant), but Failyer[4] and Alsberg and Black[5] have shown that many other plants, some of which are excellent cattle foods, contain more barium than the loco weed. Alsberg and Black report from 0.006 to 0.030 per cent BaO in various dried plants. McHargue[6] and Artis and Maxwell[7] found barium in tobacco and some other plants. The amount reported varied from 0.010 to 0.128 per cent BaO. Other investigators have reported the presence of barium in plants, but it is not necessary to continue the reference list, since it is well established that barium is a common constituent of plant ash.

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[1] Hart and Peterson, Wis. Agr. Expt. Sta., Research Bulletin No. 14 (1911). In most cases in Wolff's tables the sulphur was determined in the ash after burning. Skinner, in Bulletin No. 116, Bureau of Chemistry, U. S. Dept. of Agr. (1908), has shown that cottonseed meal and mustard-seed meal lose 90 and 92 per cent, respectively, of their sulphur when ashed.

[2] Land. Vers-Stat., 51, 473 (1899).

[3] Bul. 129, Bureau of Plant Industry, U. S. Dept. of Agr. (1908).

[4] Bul. 72, Bureau of Soils, U. S. Dept. of Agr. (1910).

[5] Bul. 246, Bureau of Plant Industry, U. S. Dept. of Agr. (1912).

[6] J. Am. Chem. Soc., 35, 826 (1913).

[7] Chem. News, 114, 62 (1916).

CAESIUM.

Von Lippmann[1] found caesium in the ash of the sugar beet.

CHROMIUM.

The ash of the Scotch fir, silver fir, some vines, poplar, and hornbeam was found by Demarcay[2] to contain spectroscopic traces of chromium. Jorissen[3] found chromium in a sample of coal from Liege. While this may have been originally in plant remains, there is doubt about it, for the same author found chromium in the shales in which the coal was interbedded.

LITHIUM.

Gaunersdorfer[4] studied the poisoning of plants by lithium salts and found that lithium is a fairly constant but not an essential constituent of some plants.

Tschermak[5] found spectroscopic amounts of lithium in a large number of plants, though in some kinds it did not appear to be present. It appeared more strongly in the leaves and small stems. Voelker[6] found that an application of 200 pounds of Li_2O to the acre was more beneficial than potash fertilization. Contrary to this experience, Ravenna and Zamorani[7] found lithium salts injurious to tobacco and poisonous to beans and oats.

MOLYBDENUM.

Demarcay[8] reports spectroscopic amounts of molybdenum in vines, fir, oak, hornbeam, and poplar. Jorissen[8] detected it in coal from Liege.

RUBIDIUM.

Pfeiffer[9] found 1.75 grams rubidium chloride per kilogram of ash from sugar beets. This element was also found in tobacco by the same author. Loew[10] states that small amounts of rubidium chloride gave increased yields of Chinese cabbage, barley, and spinach.

STRONTIUM.

Haselhoff[11] states that strontium is taken up by plants and appears to replace calcium when there is an insufficient supply of that element. In water-culture experiments larger amounts of strontium salts are poisonous.

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[1] Ber., 21, 3492 (1888).
[2] Compt. Rend., 130, 91 (1900).
[3] Bul. Sci. Acad. Roy. Belg., 178 (1905).
[4] Landw. Vers.-Stat., 34, 171 (1887).
[5] Zeit. Landw. Versuchsw., 2, 560 (1899).
[6] J. Roy. Agr. Soc., 65, 306 (1904).
[7] Atti. Accad. Lincei. (5), 2, 626 (1909).
[8] Loc. cit.
[9] Arch. Pharm. (2), 150, 97.
[10] Bul. Col. Agr. Tokyo, Imp. Univ., 5, 461 (1903).
[11] Landw. Jahrb., 22, 851 (1893).

TITANIUM.

According to Salm-Horstmar,[1] titanium may exist in the ash of barley and oats.

VANADIUM.

Bechi[2] found vanadium in various plants, especially those growing on clay soils. It was present in grasses growing on Etna lava in quantities too small to estimate. Its occurrence in plants is regarded as being due to its ismorphism with phosphoric acid. Coals from Belgium and Peru have been found to contain vanadium. Demarcay[3] detected traces of vanadium in vines, fir, poplar, and hornbeam. Ramirez[4] states that vanadium is absorbed and stored by some plants and causes anomalies in their growth.

ZIRCONIUM AND RARE EARTHS.

No mention is made of the occurrence of these elements in plant ash. Three plants only were tested for zirconium and the rare earths in this work.

SELECTION AND PREPARATION OF THE SAMPLES.

So far as it was practicable, the plants selected for this work had grown on soil that previously had been analyzed in these laboratories, and the plant samples were taken as near as possible to the spot where the soil sample had been taken. In selecting plants consideration was given to the fact that there are variations in the composition at different stages of growth and also to the fact that rain water falling on growing plants leaches out no inconsiderable amount of soluble inorganic plant constituents and returns them to the soil. The plants were selected with as much uniformity as possible, the aim being to gather them when in bloom. In all cases, except when otherwise stated, the entire part of the plant above ground was taken for analysis. The majority of the samples were gathered during the latter part of June, 1915. Important crop plants would have been preferred to some of the trees and waste-land grasses, but some soils that had previously been analyzed did not support such crops, so trees and weedlike plants were used. In beginning the investigation it was hoped to study the composition of the same kind of plants grown on soils differing widely in composition; for instance, to compare the lime content of red clover grown on a Hagerstown loam having 0.93 per cent CaO with red clover grown on a York silt loam having 0.08 per cent CaO. No legumes whatever could be found growing on the latter soil, a fact which in itself is significant.

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[1] Johnson, "How Crops Grow," p. 137. New York (1890), Orange Judd Co.
[2] Atti. Accad. Lincei (3) (Mem. Sci. Fis. Mat. e Nat.) 3, 403 (1878–79).
[3] Loc. cit.
[4] Anales. Soc. Quim., Argentina (2), 6, 145 (1914).

The green weights of the samples were not taken. On receipt at the laboratory the samples were air dried at a slightly elevated temperature, ground, and stored in stoppered bottles. The proper grinding of the samples presented many difficulties. An Excelsior coffee mill was found the most efficient machine for the purpose, but the plant fiber in many cases was so tough and leathery that there was always a contamination by the material of the grinder.[1]

For determinations like sulphur, chlorine, and the alkalies, where a small sample was taken for analysis, the material was ground finer in an agate or porcelain mortar.

There was some foreign material in the samples, mostly soil grains adhering to the majority of plants. Nearly all of this material could be removed by brushing and picking, though some of it had to be separated chemically, as described later. The ash of most plants is low in silica, consequently an admixture of even a small quantity of silica from the soil is to be avoided in this case, whereas it would make little difference in ground-rock samples.

DESCRIPTION OF THE SAMPLES.

LEGUMES.

1. *Alfalfa.*—One-half mile west of Penn Square, Norristown, Pa. Soil, Penn silt loam. This sample was 2 feet high and in bloom when cut.

2. *Alfalfa.*—One mile north of Conshohocken, Pa. Soil, Hagerstown loam. This sample had not bloomed when cut.

3. *Alfalfa.*—Stein farm, Carollton, Mo. Soil type not determined. This sample was mature. It had some fine sand adhering to it so persistently that it was impossible to brush or pick it all off.

4. *Beans.*—String variety. Two and one-half miles northwest of Charlotte, N. C. Soil, Cecil clay. The plants were about 2 feet high and contained blossoms and small pods. There was a heavy rain in the locality just before the plants were gathered, and it was impossible to remove all the soil that had been splashed on the lower leaves.

5. *Beans.*—Seeds of the string variety. Three miles east of Marlboro, N. H. Soil, Gloucester stony loam.

[1] The iron particles ground off of the machine were very efficiently removed by sliding the sample through a soft iron trough which was in contact with a powerful magnet.

As a check on the efficiency of this treatment, the following test was made: A sample of beans (seeds) was coarsely ground, then sampled and analyzed for iron. A subsample was passed several times through the mill, then run over the iron trough and analyzed for iron. A contamination of 5 milligrams Fe_2O_3 to 100 grams of bean meal was noticed. Reckoned on the dry basis, this amounts to 0.005 per cent. The grinding of this particular sample was more severe than with ordinary samples, and it can be safely assumed that the contamination of iron in the samples reported was well under 0.005 per cent. In the figures given in the tables no attempt is made to correct for this contamination.

6. *Clover, Crimson.*—Three and one-half miles southwest of Charlotte, N. C. Soil, Cecil sandy loam. This sample was in full bloom.

7. *Clover, Red.*—One-half mile west of Penn Square, Norristown, Pa. Soil, Penn silt loam. This sample was in bloom.

8. *Clover, Red.*—One mile northwest of Conshohocken, Pa. Soil, Hagerstown loam. Sample was in bloom.

9. *Clover, Red.*—Three miles east of Marlboro, N. H. Soil, Gloucester stony loam. These plants were mature and the stems frequently carried both blossoms and seeds.

10. *Clover, Sweet.*—One mile northwest of Conshohocken, Pa. Soil, Hagerstown loam. This sample was 4 feet tall, but had not commenced to bloom.

11. *Clover, White.*—One mile northwest of Conshohocken, Pa. Soil, Hagerstown loam. This sample had just commenced to bloom. There was not enough of the sample to complete the analysis.

12. *Clover, White.*—One hundred yards south of derrick, Mount Mica, Paris, Me. Soil type not determined. This sample was gathered about the middle of August when many of the blossoms had seeded. It was not cultivated, but grew in a place formerly occupied by a horse sweep.

13. *Peas, smooth-seeded variety.*—Two and one-half miles northwest of Charlotte, N. C. Cecil clay. This sample contained blossoms and partly matured peas. There was some unavoidable contamination on the lower leaves.

VEGETABLES AND MISCELLANEOUS CROPS.

14. *Apples, fruit, variety Baldwin.*—Three miles east of Marlboro, N. H. Soil, Gloucester stony loam. It was quite difficult to dry this sample enough to be ground. A moisture determination was made on the partially dried sample, then the whole sample was dried at about 150° C. until it became crisp enough to grind. The total loss in weight was recorded, and a suitable correction applied in calculating the results.

15. *Beets.*—Tubers only. Three miles east of Marlboro, N. H. Soil, Gloucester stony loam. This sample had been stored in a cellar over winter. The small amounts of silica, iron, and aluminum show that there was little soil contamination.

16. *Cabbage.*—Two and one-half miles northwest of Charlotte, N. C. Soil, Cecil clay. This sample was a small head, weighing about a kilogram, and the upper part of the stem.

17. *Carrots.*—Tubers only. Three miles east of Marlboro, N. H. Soil, Gloucester stony loam. This sample was stored in a cellar over winter.

18. *Cotton.*—Plant. Three miles southwest of Laurinburg, N. C. Soil, Norfolk sandy loam. These plants were a little over two feet high and were nearly ready to bloom.

19. *Lettuce.*—One-half mile west of Penn Square, Norristown, Pa. Soil, Penn silt loam. This sample was taken after the lettuce had grown tall preparatory to seeding.

20. *Onions.*—Bulbs only. Three miles east of Marlboro, N. H. Soil, Gloucester stony loam. It was impossible to dry this sample to constant weight. After 120 hours of drying at 105° there was still a loss in weight.

21. *Potatoes, Irish.*—Tubers only. Three miles east of Marlboro, N. H. Soil, Gloucester stony loam. Great care was taken to wash the depressions and eyes of the tubers free from soil.

22. *Potatoes, sweet.*—Vines. Three miles southwest of Laurinburg, N. C. Soil, Norfolk sandy loam. These vines were young and had fleshy tips.

23. *Tobacco.*—One and three-fourths miles northeast of Archer, N. C. Soil, Durham sandy loam. The stalks were three and one-half feet high. It had not bloomed.

24. *Tomato.*—Vines. Three miles southwest of Laurinburg, N. C. Soil, Durham sandy loam. The growth was rather small. Flowers and small fruits had formed on the plant.

GRASSES.

25. *Bluegrass.*—One-eighth mile west of Penn Square, Norristown, Pa. Soil, Penn silt loam. The growth was luxuriant. The samples taken were in seed.

26. *Broom sedge.*—Three-fourths mile east of Kings Mountain Battleground, Bethany, S. C. Soil, York silt loam. Small shoots, not in bloom.

27. *Corn.*—Stalks and leaves. Three miles southwest of Laurinburg, N. C. Soil, Norfolk sandy loam. The plants were young and had reached a height of about 4½ feet.

28. *Corn.*—Stalks and leaves. Three-fourths mile east of Kings Mountain Battleground, Bethany, S. C. Soil, York silt loam. The growth was light. The plants were 2 feet high when cut.

29. *Oats.*—Straw with grain. One-half mile west of Penn Square, Norristown, Pa. Soil, Penn silt loam. Heavy yield. The grain was in the milk when cut.

30. *Orchard grass.*—One-half mile west of Penn Square, Norristown, Pa. Soil, Penn silt loam. These plants had just seeded.

31. *Timothy.*—One-half mile west of Penn Square, Norristown, Pa. Soil, Penn silt loam. This sample was cut in bloom.

32. *Timothy.*—One mile northwest of Conshohocken, Pa. Soil, Hagerstown loam. This sample was in bloom.

33. *Timothy.*—Three miles east of Marlboro, N. H. Soil, Gloucester stony loam. Large plants in late bloom.

34. *Timothy.*—One hundred yards southwest of derrick, Mount Mica, Paris, Me. Poor growth, in seed and partly dried.

35. *Wheat.*—Straw with grain. One and three-fourths miles northeast of Archer, Johnson County, N. C. Soil, Durham sandy loam. This sample had made a poor growth.

36. *Wheat.*—Straw with grain. One-half mile west of Penn Square, Norristown, Pa. Soil, Penn silt loam. There was a good yield in the field where this sample was taken.

TREES AND BUSHES.

37. *Birch, White.*—Leaves only. Beryl Mountain, Acworth, N. H. This bush was growing in a cavity where a large amount of beryl had been taken out. The soil was largely made up of broken beryl. Weight of leaves, 62.9 grams.

38. *Birch, White.*—Stems only. Same locality as above. Weight of stems, 88.6 grams.

39. *Oak, Blackjack.*—Three-fourths mile east of Kings Mountain Battleground, Bethany, S. C. Soil, York silt loam. Entire bush, about 3½ feet high.

40. *Oak, Post.*—Three-fourths mile east of Kings Mountain Battleground, Bethany, S. C. Soil, York silt loam. Entire small tree, about 4 feet high.

41. *Oak, White.*—One and one-fourth mile southeast of Trevilians, Va. Soil, Louisa loam. Entire bush, about 4 feet high.

42. *Oak, White.*—One and three-fourths miles northeast of Archer, Johnson County, N. C. Soil, Durham sandy loam. Small tree, about 5 feet high. Weight of leaves, 124.1 grams.

43. *Oak, White.*—Stems. Location and soil same as No. 42. Weight of stems, 194.5 grams.

44. *Pine, Shortleaf.*—Needles. One and one-fourth miles southeast of Trevilians, Va. Soil, Louisa loam. Weight of needles, 157.1 grams.

45. *Pine, Shortleaf.*—Stems, short. Location and soil same as No. 44. Weight of stems, 134.3 grams.

46. *Pine, Longleaf.*—Needles. One and three-fourths miles northeast of Archer, N. C. Soil, Durham sandy loam. Weight of needles, 273.3 grams.

47. *Pine, Longleaf.*—Stems. As above. Weight of stems, 179.5 grams.

48. *Raspberry (wild red).*—Vines. Growing on the edge of a beryl dump on Beryl Mountain, Acworth, N. H.

ANALYTICAL RESULTS.

The results of analyses of plant ash are given in Tables I to IV, and the analyses of soils on which samples grew in Table V.

TABLE I.—*Results of chemical analyses of plant ash: Legumes.*

[Expressed in per cent of material dried in oven at 105°.]

Element.	No. 1. Alfalfa.	No. 2. Alfalfa.	No. 3. Alfalfa.	No. 4. Beans (plant).	No. 5. Beans (seeds).	No. 6. Clover.	No. 7. Clover.	No. 8. Clover.	No. 9. Clover.	No. 10. Clover.	No. 11. Clover.	No. 12. Clover.	No. 13. Peas.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
SiO_2	0.065	0.075	[1] 1.50	[1] 0.82	0.002	0.238	0.165	0.171	0.102	0.064	0.441	0.066	[1] 0.250
TiO_2	.001	.001	.011	.005	Trace.	.003	.002	.002	.002	.005	.002	Trace.	.008
Al_2O_3	.068	.007	[2] .306	[2] .215	.002	.062	.023	.005	.038	.009	.093	N. F.	[2] .201
Fe_2O_3	.039	.041	.090	[2] .135	.012	.047	.057	.070	.023	.039	.083	.034	[2] .177
MnO	.0071	.0048	.0075	[2] .0124	.002	.005	.007	.0037	.006	.0024	.0046	.0113	.008
Cr_2O_3	N. F.	N. F.	N. F.	Trace.	N. F.	N. F.	N. F.	N. F.	.0008	N. F.	N. F.	Trace.	Trace.
V_2O_5	N. F	N. F.	N. F.	Trace.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	Trace.	Trace.	N. F.
MoO_3	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.
CaO	2.72	2.50	2.35	2.90	1.64	1.58	2.90	2.92	2.03	1.67	2.22	1.15	1.69
BaO	.008	.002	.015	.019	.0003	.012	.0082	.006	.006	.003	.0015	.008	.007
SrO	.006	.005	.023	.005	N. F.	N. T.	.014	N. T.	.004	.010	N. T.	.005	.006
MgO	.715	.700	.889	.670	.292	.482	1.12	.785	.602	.485	.720	.560	.300
K_2O	1.46	2.53	2.92	3.65	1.71	2.85	1.59	2.38	1.84	2.45	N. T.	4.71	3.32
Na_2O	.36	.26	.14	.14	.01	.11	.11	.10	.01	.09	N. T.	.12	.20
Li_2O	.000003	.00001	.00003	.00008	.00003	.000005	.00003	.00002	.00005	.000015	N. T.	.00004	.00004
Rb_2O	.0018	.0013	.005	Trace.	.0025	.0006	.00065	.0008	.015	.00065	N. T.	.008	Trace.
Cs_2O	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. T.	N. F.	N. F.
P_2O_5*	.473	.861	.588	.690	.990	.647	.520	.566	.392	.519	.709	.680	.680
SO_3*	1.01	.21	.78	.76	.54	.55	.48	.48	.40	1.76	N. T.	.63	.83
Cl*	.18	.35	.11	.86	.07	.37	.20	.20	.297	.28	N. T.	.48	.83
H_2O at 105°	7.06	10.80	8.36	8.90	10.20	6.62	8.26	7.26	9.14	6.64	7.00	8.30	9.59
Mineral constituents by addition	7.1	7.5	9.7	10.9	5.3	6.9	7.2	7.7	5.7	7.3	.....	8.4	8.5

[1] Some of the silica reported probably comes from fine soil on stems and leaves.

[2] High aluminum and iron content is probably due to unavoidable contamination with soil, the high MnO content of the string beans may be due to the same cause, for the soil contained 0.51 per cent MnO.

* Total P_2O_5, SO_3, and Cl in plant determined.

TABLE II.—*Results of chemical analyses of plant ash: Vegetables and miscellaneous crops.*

[Expressed in per cent of material dried in oven at 105°.]

Element.	No. 14. Apples.	No. 15. Beets.	No. 16. Cabbage.	No. 17. Carrots.	No. 18. Cotton.	No. 19. Lettuce.	No. 20.[1] Onions.	No. 21. Potatoes.	No. 22. Potato vines, sweet.	No. 23. Tobacco.	No. 24. Tomato vines.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
SiO_2	0.012	0.014	0.184	0.015	0.290	0.538	0.011	0.008	0.410	0.125	0.519
TiO_2	Trace.	Trace.	.001	.0002	.001	.003	.0004	Trace.	Trace.	.001	.002
Al_2O_3	.006	.018	.023	.012	.075	.016	.006	.007	.080	.062	.145
Fe_2O_3	.007	.015	.027	.021	.043	.117	.012	.004	.048	.054	.063
MnO	.0005	.0067	.0064	.0017	.0123	.008	.0030	.0011	.0127	.0123	.0092
Cr_2O_3	N. F.	Trace.	Trace.	N. F.	Trace.	Trace	N. F.	N. F.	Trace.	N. F.	N. F.
V_2O_5	N. F.	Trace.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.
MoO_3	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.
CaO	.056	.219	2.42	.526	4.14	3.94	.393	.040	2.71	4.88	2.88
BaO	.0003	.0006	.003	.003	.004	.008	.002	.0006	.016	.018	.008
SrO	.001	.006	.012	.004	.005	.036	.016	.001	.007	.022	.023
MgO	.067	.300	.386	.310	.926	.980	.209	.187	1.00	.646	1.11
K_2O	1.00	3.93	4.41	7.22	4.06	8.66	2.04	3.29	7.45	4.57	6.85
Na_2O	.01	.09	.24	.43	.38	.64	.20	.06	.21	.39	.41
Li_2O	.000005	.000005	.00002	.000003	.00005	N. T.	.00005	.000003	.00005	.00008	.000035
Rb_2O	.0013	.0003	.0013	0009	.0006	N. T.	.0009	.0019	.0006	.0038	.0006
Cs_2O	N. F.	P.	N. F.	N. F.	N. F.	N. T.	N. F.	N. F.	N. F.	N. F.	N. F.
P_2O_5	1.56	1.11	.890	.800	1.19	1.30	.552	.550	.920	.756	.633
SO_3	.23	.30	2.50	.38	3.53	1.14	.89	.45	1.22	1.28	4.28
Cl	.03	.71	.85	1.50	.16	1.40	.51	.57	.24	2.50	.38
H_2O at 105°	11.64	6.40	14.74	16.85	9.30	8.73	.00*	9.45	9.88	14.16	7.80
Mineral constituents by addition	3.0	6.7	11.9	11.2	14.8	18.7	4.8	5.1	14.3	15.3	17.3

[1] All figures are calculated on the air-dry weight.

TABLE III.—*Results of chemical analyses of plant ash: Grasses.*

[Expressed in per cent of material dried in oven at 105°.]

Element.	No. 25. Bluegrass.	No. 26. Broom sedge.	No. 27. Corn plant.	No. 28. Corn plant.	No. 29. Oat plant.	No. 30. Orchard grass.	No. 31. Timothy.	No. 32. Timothy.	No. 33. Timothy.	No. 34. Timothy.	No. 35. Wheat plant.	No. 36. Wheat plant.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
SiO_2	2.72	2.28	1.10	0.99	2.10	4.40	3.19	1.58	0.784	1.29	2.17	2.50
TiO_2	.002	Trace.	.003	.017	.001	.0004	.003	.002	.001	Trace.	.002	.004
Al_2O_3	.050	.042	.030	.012	.033	.048	.069	.049	.041	.024	.181	.173
Fe_2O_3	.025	.029	.022	.037	.022	.053	.041	.034	.022	.038	.020	.045
MnO	.0037	.0157	.012	.010	.0150	.024	.005	.0047	.008	.0145	.0232	.0061
Cr_2O_3	Trace.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	.004	N. F.	N. F.	N. F.
V_2O_5	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.
MoO_2	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.
CaO	.264	.296	.654	.660	.418	.412	.369	.342	.285	.270	.141	.201
BaO	.004	.006	.007	.002	.002	.008	.004	.003	.005	.002	.002	.002
SrO	.002	.003	.003	.007	.008	.006	.001	.002	.003	.002	.003	.002
MgO	.191	.220	.376	.420	.379	.449	.243	.262	.154	.110	.227	.237
K_2O	2.49	2.04	3.37	4.22	2.65	2.97	2.50	2.11	1.97	1.90	1.26	1.02
Na_2O	.02	.09	.07	.13	.47	.03	.01	.03	.01	.10	.03	.05
Li_2O	.000075	.00002	.00005	.00005	.000045	.00008	.00002	.000015	.00006	.00001	.000005	.000025
Rb_2O	N. F.	N. F.	.001	Trace.	.0009	.0006	N. F.	N. F.	.025	.01	.0003	N. F.
Cs_2O	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	.001	N. F.	N. F.
P_2O_5	.686	.415	.593	.464	.768	.591	.545	.483	.395	.35	.877	.602
SO_3	.47	.38	.51	.55	.71	1.01	.48	.68	.22	.41	.54	.33
Cl	.44	.28	.19	.70	.74	.52	.71	.54	.50	.59	.23	.31
H_2O at 105°	9.64	7.37	13.98	12.3	8.44	10.0	7.71	9.47	7.90	9.96	10.67	8.54
Mineral constituents by addition	7.3	6.1	6.9	8.2	8.3	0.5	8.1	6.1	4.4	5.1	5.7	5.5

TABLE IV.—*Results of chemical analyses of plant ash: Trees and bushes.*

[Expressed in per cent of material dried in oven at 105°.]

Element.	No. 37, birch leaves.	No. 38, birch stems.	No. 39, oak.	No. 40, oak.	No. 41, oak.	No. 42, oak leaves.	No. 43, oak stems.	No. 44, pine needles.	No. 45, pine stems.	No. 46, pine needles.	No. 48, pine stems.	No. 48, raspberry vines.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
SiO_2	0.050	0.030	0.071	0.075	0.310	0.222	0.024	0.170	0.014	0.528	0.045	0.018
TiO_2	Trace.	N. F.	Trace.	Trace.	N. F.	Trace.	Trace.	.0001	.0001	Trace.	Trace.	Trace.
Al_2O_3	.024	N. F.	.033	.082	.011	.038	.070	.253	.090	.187	.063	.077
Fe_2O_3	.029	.015	.025	.024	.018	.023	.020	.020	.016	.021	.025	.017
MnO	.0655	.0098	.070	.131	.049	.160	.0393	.0596	.011	.0642	.0113	.304
Cr_2O_3	N. F.	N. F.	N. F.	N. F.	N. F.	Trace.	N. F.	Trace.	N. F.	Trace.	N. F.	Trace.
V_2O_5	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	Trace.	N. F.	Trace.	N. F.	N. F.
MoO_2	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.
CaO	1.45	.440	.95	1.36	1.85	1.14	1.25	.320	.240	.434	.230	1.11
BaO	.012	.005	.064	.016	.012	.015	.020	.005	.007	.005	.006	.004
SrO	.006	.004	.022	.020	.004	.013	.023	.003	.004	.011	.004	.002
MgO	.55	.170	.389	.348	.300	.72	.18	.210	.130	.415	.129	.78
K_2O	1.99	.58	1.55	.58	.65	.91	.34	.91	.30	.98	.71	1.19
Na_2O	.10	.13	.12	.01	.11	.13	.15	.07	.07	.15	.13	.22
Li_2O	.000047	.00003	.00006	.0000065	.000005	.00015	.000003	.00006	.0001	.00002	.0000065	.00002
Rb_2O	.001	.0003	N. F.	Trace.	.00015	.000012	.0015	.00015	N. F.	.00063	.0004	.01
Cs_2O	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	.001
P_2O_5	1.10	.33	.400	.146	.146	.261	.274	.27	.075	.221	.121	.64
SO_3	.35	.16	.30	.22	.14	.35	.16	.42	.14	.16	.18	.13
Cl	.12	.04	.04	.33	.08	.06	.05	.11	.05	.13	.09	.12
H_2O	8.68	7.80	8.26	6.77	10.40	7.74	6.68	7.2	8.4	7.60	7.18	10.1
Mineral constituents by addition	5.8	1.9	4.0	3.3	3.6	4.0	2.6	2.8	1.1	3.3	1.7	4.6

TABLE V.—*Showing the chemical composition of certain soils from which plants were gathered.*

[Analyses by W. O. Robinson.]

Element.	Norfolk sandy loam, 0″–14″, Laurinburg, N. C.	Hagerstown loam, 0″–8″, Conshohocken, Pa.	Gloucester stony loam, 0″–8″, Marlboro, N. H.	Cecil sandy loam, 0″–8″, Charlotte, N. C.	Cecil clay, 0″–6″, Charlotte, N. C.	Durham sandy loam, 0″–10″, Archer, N. C.	York silt loam, 0″–10″, Bethany, S. C.	Louisa loam, 0″–12″, Trevilians, Va.	Penn silt loam, 0″–9″, Norristown, Pa.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
SiO_2	94.50	70.99	65.68	66.49	88.57	80.79	76.71	84.58	74.33
TiO_2	.71	1.01	.79	1.02	.55	.55	.41	1.51	1.04
Al_2O_3	2.07	11.39	14.15	17.11	5.76	10.55	12.85	5.54	11.00
Fe_2O_3	.83	4.23	5.67	7.43	1.55	1.61	2.81	3.30	4.64
MnO	.007	.180	.068	.51	.044	.017	.005	.045	.136
Cr_2O_3	.004	.004	Trace.	.013	.002	.004	.007	.013	.006
V_2O_5	.01	.08	.08	.05	.01	.02	.04	.03	.03
Rare earths	.02	.08	N. T.	.02	.03	.03	.02	.04	N. T.
ZrO_2	.02	.08	.04	.003	.04	.08	.04	.08	.05
MoO_2	N. F.	N. F.	N. F.	N. F.	N. F.	P.	P.	N. F.	N. F.
NiO+CoO	Doubt.	N. T.	N. T.	.04	.03	.04	N. T.	N. T.	N. T.
CuO	N. T.	N. T.	N. T.	P.	P.	P.	N. T.	N. T.	N. T.
CaO	.39	.93	1.36	.36	.39	.89	.08	.21	1.13
BaO	.004	.060	.53	.063	.039	.112	.287	.037	.053
SrO	.02	.11	.05	.04	.01	.05	.05	.04	.04
MgO	.09	1.08	.83	.31	.21	.19	.29	.25	.69
K_2O	.10	2.71	2.16	.62	.82	3.96	3.26	.74	1.57
Na_2O	.11	.82	1.39	.16	.16	.87	.39	.14	1.53
Li	P.	P.	P.	P.	P.	P.	P.	P.	P.
Rb	.001	.002	.002	Trace.	.001	.01	.001	.001	.002
Cs	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.
P_2O_5	.06	.19	.15	.17	.08	.12	.05	.12	.16
SO_3	.07	.39	.17	.07	.04	.06	.12	.15	.15
Ignition loss	1.74	6.08	9.52	8.06	2.93	1.41	3.16	3.89	4.51
Water at 110°	.48	1.61	3.39	2.47	.53	.48	.47	.92	1.72
Organic matter	1.13	2.87	7.07	1.26	1.46	.40	1.78	2.40	1.99
CO_2 from carbonates	N. F.	.33	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.	N. F.

N. T., not tested. N. F., not found. P., present.

[1] Taken from Bul. 122, Dept. Agriculture (Professional paper).

The results given in these tables are calculated on the moisture-free basis except in cases noted. The total percentage of ash has not been given. It is not practicable to weigh ash on account of its hygroscopic nature, the particles of unburned carbon present, and the variable amount of carbon dioxide present. It is almost impossible to burn to a white ash plants that are high in silica without volatilizing some of the constituents. The silica probably forms a slag with the fluxing alkalies and coats particles of unburned carbon, protecting it from further action.

As an approximation to the total ash the sum of the mineral constituents is given. These figures are comparable to other results given for ash, except that carbon dioxide is not included and that partial correction has been made for the soil grains adhering to the plant. Many published tables show the percentage of a certain constituent in the ash, and the results here published may be compared with such data by taking the sum of the mineral constituents to represent the ash. For example, in Table I, sample No. 1, alfalfa, there is 1.46 per cent of potash in the thoroughly dried plant, and, taking the sum of the mineral constituents to represent the ash, there would be 20.56 per cent of potash in the ash.

Manganese in plants varies more in amount than most of the other elements. It appears to concentrate in the leaves, as shown in the case of the pine and oak samples. The presence of more than 0.3 per cent of MnO in the raspberry plant from Acworth, N. H., is remarkable, and the question arose whether all raspberry bushes and like plants were high in manganese. Two samples, one of raspberry bushes and one of rambler roses from Vienna, Va., were collected and analyzed. The Blackcap raspberry bushes showed 0.062 per cent of MnO, and the rambler roses, stem and leaves, contained 0.019 per cent. This would indicate that members of the rose family contain more manganese than the average of plants. White[1] has found from 0.108 to 0.153 per cent of Mn in sorrel plants, and from 0.059 to 0.085 per cent of Mn in clover plants.

There is wide variation in the composition of the same plant. Some of this variation may be due to the different stages of growth, but the greater part of it would seem to be due to the composition of the soil. For instance, caesium was found in plant ash from Acworth, N. H., and Paris, Me. Caesium beryls are known to occur in both these localities. Shorey[2] reports an extreme variation of the composition of plant ash due to the difference in amounts of lime found in two soils. He writes:

In the case of the fiber from Sisal Plantation, where the soil was a disintegrated coral, 40 per cent of the ash was lime, while in that from the experi-

[1] Ann. Rept. Pa. State College Agr. Expt. Sta. (1913–14), p. 46.
[2] Bul. 13, Hawaii Agr. Expt. Sta. (1906).

ment station, where the soil contains less than 1 per cent lime, the amount in the sisal ash was but 7 per cent.

White[1] found considerable variation of the lime content of clover grown in soils of different reaction. The figures are as follows: Alkaline, 3.02 per cent Ca; neutral, 2.68 per cent Ca; and acid; 2.67 per cent Ca.

The attention of the bureau has frequently been called to instances of clovers and alfalfas growing on acid soils. In one such case at Carrollton, Mo., samples of alfalfa were submitted that had been growing luxuriantly on an apparently acid soil for eight years. The growth exceeded that of some alfalfa fields where the soil reaction was apparently more favorable. Mr. J. G. Smith, of this bureau, found the lime requirement of this soil to be 3 tons of CaO to the acre. He also found that the total lime and magnesium in the soil was much higher than the average. An examination of the tables shows that this alfalfa, No. 3, contains somewhat less lime, but more magnesium than the eastern alfalfas. It appears that in this case the alfalfa had extracted the amount of lime and magnesia necessary for normal growth from the calcium and magnesium silicates in the soil and therefore that compounds of these elements are necessary for the elaboration of plant tissue, rather than to give an alkaline reaction to the soil.

There are wide variations in the composition of the same kind of plants, and from the data here presented it can not be stated whether these are due to difference in the stage of growth or to a difference in the composition of the soil. All things considered, however, it would seem that the most profound influence the composition of the soil has on the plant is not on the composition of the plant but on the occurrence of that plant on the soil. To be concrete, it seems that a plant will not grow naturally, seeding itself year after year, on a soil where it can extract only a part of the normal amount of any element necessary for its growth. Diligent search failed to show any legumes, which are high in lime, growing on York silt loam in Bethany, S. C. This soil contains only 0.08 per cent total CaO.

It may be a mere coincidence, but in the majority of cases where the plant contains a comparatively large amount of rare alkalies, there is also an abnormal amount of manganese present. The chlorine of plants that have been cultivated is high, particularly those that are usually fertilized with commercial fertilizer. Such large amounts of chlorine may not be necessary for the elaboration of plant tissue, but it seems that chlorine and sulphuric acid act as necessary vehicles to carry the alkalies from the soil to the plant. In the cotton

[1] Ann. Rept. Pa. State College Agr. Expt. Sta., 1913–14, p. 46.

plant, lettuce, and tobacco plant, where the potash and lime are abnormally high, the sum of the sulphur and chlorine is also high.

Vernadsky [1] has shown that rubidium and caesium are widely distributed in feldspar and micas and consequently in soils. He is of the opinion that these alkalies may occur in sufficient quantities in agricultural products to affect the accuracy of potassium determinations. In so far as plants are concerned, the contention of Vernadsky does not seem to be well founded, for there were only three cases where the quantity of rubidium was large enough to be detected in the potassium determinations, and in those cases the amount of potassium would be increased by about 0.01 per cent.

The aluminum in plants varies widely. In some cases there is more aluminum than iron. It is true that a large number of errors accumulated upon this determination, but every precaution was taken to correct for impurities, and it is believed that the results are not consistently too high. Unavoidable contamination by soil would, of course, result in a figure for aluminum higher than the true one. Such contamination would be shown by a correspondingly high silica content. High results for aluminum were checked by another analyst.

The results with reference to the rarer elements may be summarized as follows:

1. Lithium was found in spectroscopic quantities in all plants examined. Rubidium was present in the majority of cases and in larger quantities than the other rare alkalies. In cases where the amount of Rb_2O in the plant equaled or exceeded 0.01 per cent, rare alkali minerals are known to occur in the soil on which the plant was grown. Caesium was found in the ash of timothy from Mount Mica, Paris, Me., the red raspberry from Beryl Mountain, Acworth, N. H., and the beets from Marlboro, N. H. Caesium beryls are known to occur in the first two localities.

2. Chromium was occasionally found, though always in very small amounts. Vanadium was detected in only six instances and likewise in traces. Molybdenum was not found by delicate chemical tests in the ash of any plant.

3. Barium was found in determinable quantities in the ash of all plants examined. Strontium was found in all samples except bean seeds.

4. Titanium was present in the ash of all plants, though in very small amounts. With two exceptions, all plants analyzed contained aluminum. The percentages of aluminum in peas, beans, one sample of alfalfa, pine needles, wheat, and tomato plants are high. The peas, beans, and alfalfa were contaminated by soil to which the high

[1] Ueber die Begleiter des Kaliums.

aluminum content probably is due. Pine needles are exceptionally high in this element.

5. There is no evidence that vanadium replaces phosphoric acid in its functions in the plant. Rubidium and caesium are apparently absorbed by the plant when they are present in the soil solution. The larger the amount present in the soil, the more will be absorbed. Lithium is apparently not acted on in this manner, for Nos. 12 and 34 did not contain an exceptional amount of lithium, though the soil contained considerable lepidolite.

6. With the exception of sulphur, chlorine, and manganese in some cases, there is no indication that the elements determined in the foregoing work, except those commonly used, need be considered in fertilizer practices.

APPENDIX.

ANALYTICAL METHODS.

Since this work is based largely on analytical data, it seems proper that the methods employed should be stated with some detail. No satisfactory method for the complete analysis of plant ash is to be found in textbooks or bulletins. The problem is one of peculiar difficulty. The inorganic composition of plants nearly resembles that of a rock phosphate, except that there is a high content of magnesium, more iron and aluminum, and occasionally large amounts of manganese. Obviously some method which would remove the phosphoric acid early in the analysis and leave no objectionable precipitant in solution would be the ideal procedure. The basic acetate method for the precipitation of the iron group had to be discarded on account of the tendency of the small amount of iron and aluminum phosphate to run through the filter.

Treadwell and Hall have outlined a method whereby the phosphoric acid is precipitated with molybdic acid in the usual manner and the iron and aluminum separated by ammonia and ammonium sulphide, which does not precipitate the molybdenum. Test analyses made on synthetic solutions showed that iron and aluminum were not completely precipitated by this treatment, and the method was abandoned as unsatisfactory.

The phosphoric acid may be removed by silver salts in slightly acid solutions, but the coprecipitation of iron renders this separation useless.

The stannic acid made by dissolving tin in a nitric-acid solution containing a phosphate will precipitate the phosphoric acid as tin phosphate, and no tin remains in solution. Unfortunately, iron is precipitated with the tin, so the method could not be used.

After a number of trials it became evident that the method which calls for the separation of calcium as sulphate by alcohol, after the removal of silica, was the best available. Test analyses by two analysts on synthetic mixtures showed this method to be accurate. It is outlined in Mellor's, "A Treatise on Quantitative Inorganic Analysis," p. 606, J. B. Lippincott Co., Philadelphia (1913).

This method was found satisfactory after modification; that is, the removal of the iron precipitated with the calcium sulphate and the recovery of magnesium from the iron group after the precipitation of phosphoric acid, by the use of citric acid and ammonium phosphate.

SILICA.

It is impossible to prepare plants for analysis in such a manner as to have them free from contaminating soil, which is made up largely of silica. An approximate way of determining silica is carried out by digesting the dehydrated silica and sand with a solution of sodium carbonate and hydroxide as outlined in Bul. 107, of the Bureau of Chemistry. The finely divided silica of constitution dissolves, and the soil grains are supposed to resist attack. It is difficult to obtain results by this method which agree well, particularly when working with plants high in silica. For the separation of silica, two evaporations with an intervening filtration were invariably made.

THE CALCIUM PRECIPITATION.

The calcium sulphate precipitated by alcohol frequently contains iron but never phosphorus, provided, of course, the washing has been thorough. It has been our practice to dissolve the calcium sulphate in hydrochloric acid and precipitate the iron, if any, with ammonia and add it to the main precipitate. When the final volume of the alcoholic solution in which the calcium-sulphate precipitation was made is from 150 c. c. to 200 c. c. from one to two milligrams of calcium sulphate remain in solution. This was shown by the test analysis of synthetic test solutions.

THE IRON AND ALUMINUM GROUP.

The skill of the analyst is put to a severer test in making this group separation than at any other stage of the analysis. The precipitation must be quickly and completely made and the filtration hastened with all possible dispatch. This is to avoid the coprecipitation of magnesium phosphate. To this end a small but known excess of ammonia is quickly added to the hot mixture. The solution is then boiled a minute or so and the filtration made by suction in a

hot-water jacketed funnel. If there is not too much magnesium present these precautions will enable the analyst to obtain a precipitate free from magnesium or nearly so. The presence of magnesium ammonium phosphate in the iron group can easily be recognized by the appearance of crystals on the side of the beaker. When such precipitate appears it is best to complete the filtration and make a second precipitation. In this way the amount of magnesium is so reduced that it will seldom give further trouble. The washing is best done with hot water containing 5 per cent NH_4Cl. After complete washing water containing NH_4NO_3 is used to wash out the chloride prior to ignition. Some electrolyte must be used in the wash water, otherwise the phosphates of iron and aluminum will run through the filter.

Correction for the magnesium which may be in the iron group was made in the following manner: After the titanium has been determined and the phosphoric acid precipitated 1 to 2 grams of citric acid are added to the solution and the magnesium precipitated with an orthophosphate and ammonia. A correct figure for aluminum can be certain only after this magnesium correction has been made. In cases where the manganese is below or only slightly above 0.01 per cent none will be found precipitated with the iron group, nor is it necessary to correct the magnesium precipitate for such an insignificant amount. When the manganese is high, as in the raspberries, pine needles, and oak leaves, corrections are necessary. A simple colorimetric determination of the manganese in the magnesium pyrophosphate gives data enabling the analyst to give a correct figure for magnesium. Correction is made for the aluminum in the following manner: The solution of the iron group, after the titanium has been determined and the phosphoric acid has been removed, is divided into two portions; in one the manganese is estimated colorimetrically and the magnesium correction is made in the other half.

The precipitation of the magnesium and phosphoric acid in the separate halves of the filtrate from the iron group is done in the ordinary manner.

THE ALKALIES.

Great care must be used in ashing the plants, particularly when the rare, more volatile alkalies are to be determined. Potash is lost when present as the chloride, if the temperature of ignition be carried above a dull redness, barely discernable in the dark. In order to control this temperature of ignition, a special electric muffle was constructed. When the temperature, as measured by a pyrometer on the inside of the furnace and not touching the walls, did not exceed 525° C., there was no loss of potash during ashing. This fact was established by comparing analyses of the same plant made using and

omitting sulphuric acid during the ignition. In this laboratory, where the voltage of the electric current varies considerably, the very frequent attention of the analyst is required to operate the rheostat of the electric furnace in order to keep the temperature approximately uniform. The difference in radiation from the furnace on

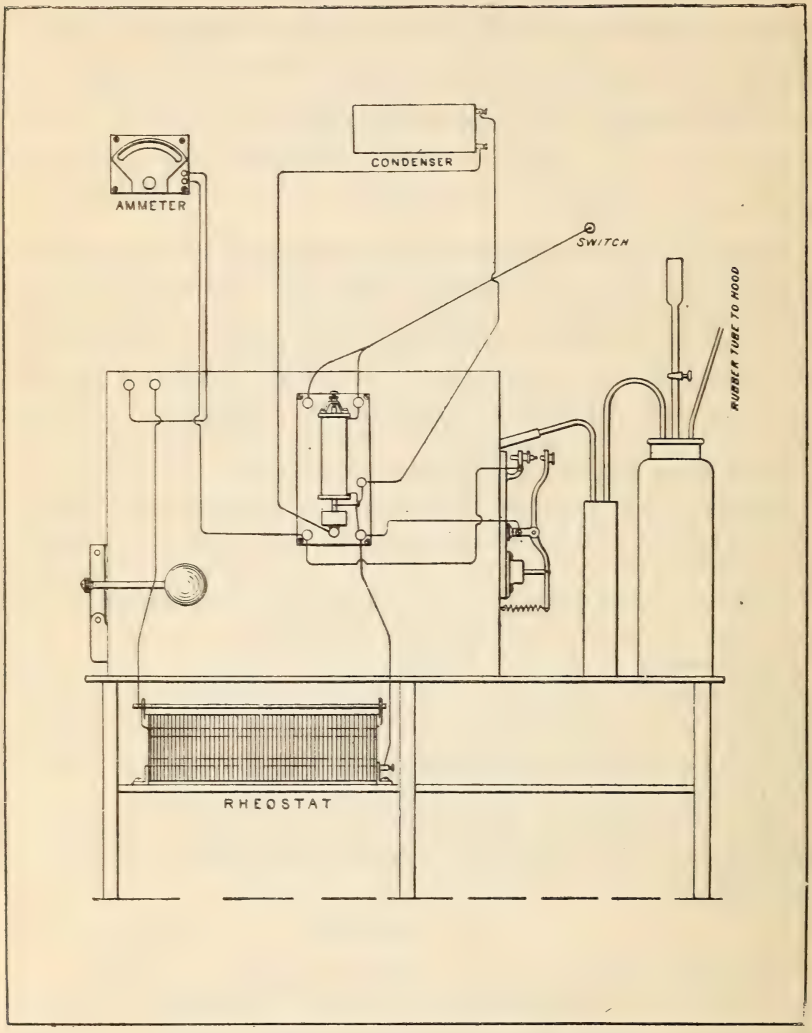

FIG. 1.—Diagram of electric furnace, side view.

hot and cold days is another factor which causes variation in temperature when the rheostat is set at the same place. To secure a fairly constant temperature without the element of guesswork, a furnace with a temperature regulator was designed. A sketch is given in figs. 1, 2, and 3.

The essential part of the automatic control is a couple consisting of a quartz tube closed at one end, inside of which is placed a nickel rod. The difference in the thermal expansion of nickel and silica is

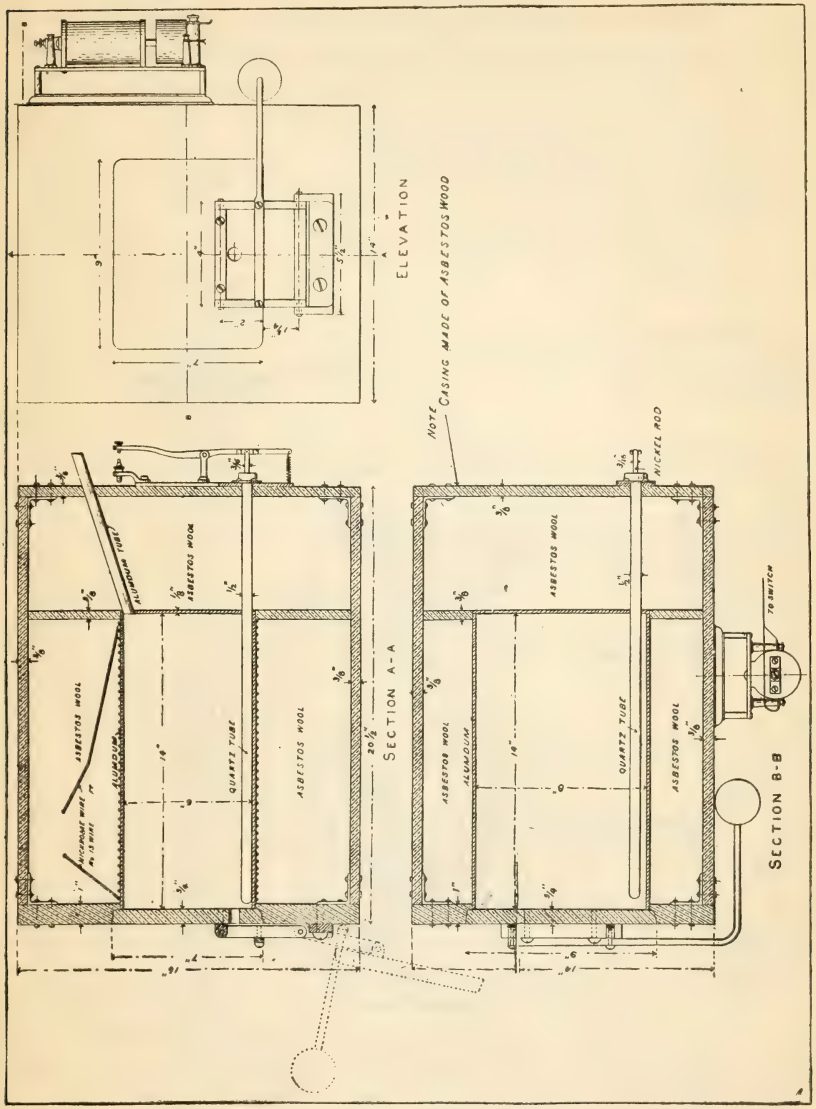

FIG. 2.—Sectional view of electric furnace.

considerable. By this device a movement of 0.01 inch for every $2\frac{1}{2}°$ C. was obtained. No change in temperature of the oven running at 525° C. could by observed with a pyrometer graduated in 5-degree intervals.

THE ELECTRIC FURNACE.

The inner case of the furnace is made of alundum on which is wound nichrome wire of 0.072-inch diameter. The resistance of the furnace is 12 ohms. At the rear an alundum tube is inserted to lead off the volatile matter to a cooling cylinder of metal which is con-

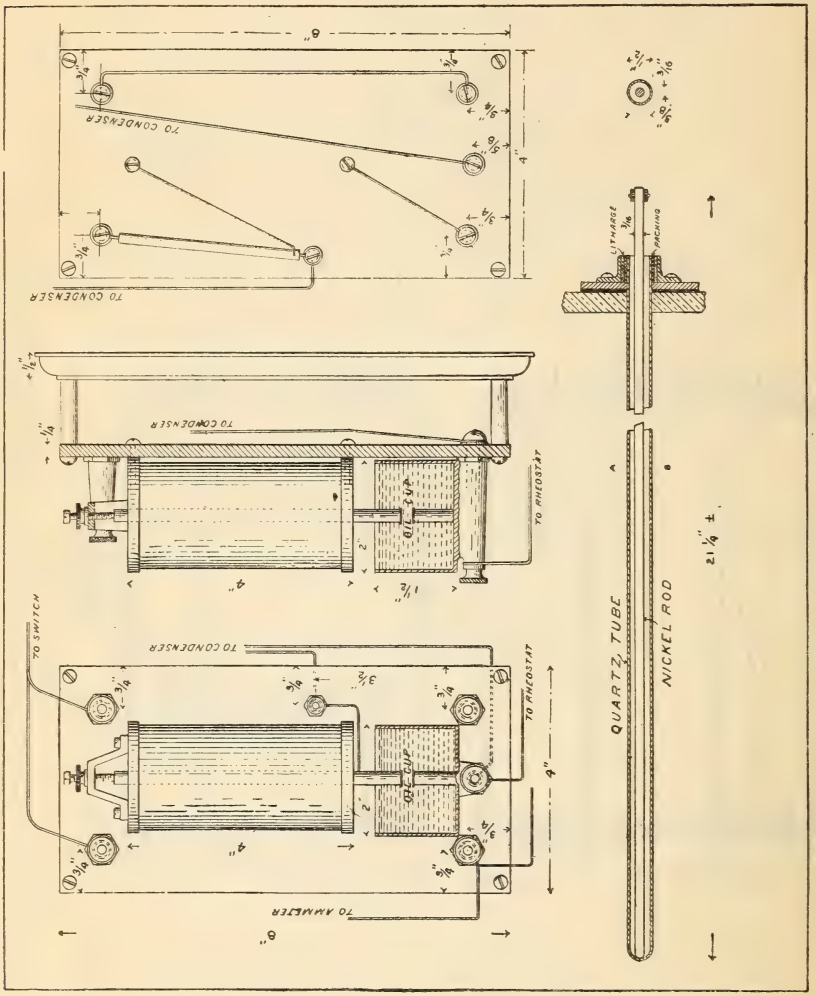

FIG. 3.—Details of regulating devices.

nected to a bottle containing water and small pieces of pumice. The other opening of the bottle is connected with the suction. Asbestos wool forms the insulating material between the alundum case and the asbestos-board outer form. The door of the furnace is mounted with double hinge and weighted to remain open or closed, as placed.

The temperature of the furnace is controlled through the action of the nickel rod which is placed inside a quartz tube. The quartz tube was fastened at the rear of the furnace to the inside of a brass piece by means of glycerine and litharge cement, after the end of the tube had been wound with asbestos cord. The other end of the lever connected with the nickel rod makes and breaks the current operating the relay. A condenser is connected with opposite sides of the gap to reduce arcing. The platinum-tipped contact pieces are also immersed in oil, which further reduces arcing tendencies. An ammeter and rheostat are connected in series with the furnace. When started with a current of 12 amperes (at 220 volts) the furnace requires about an hour and a half to reach a temperature of 500° C., after which the temperature may be kept constant with a current of 7 amperes, which is easily handled by the relay.

The time required for ashing of different plants varies considerably. Three hours is generally sufficient. The contents of the ashing dish were turned to expose unburned portions when necessary. Many times one incineration was sufficient for complete ashing, but generally all plants high in silica required a second heat treatment after leaching with water. The silica apparently forms a slag with the alkalies and protects enmeshed particles of carbon from the action of the oxygen.

It was found more convenient to determine the sodium and potassium in the same portion that was taken for the major constituents. The ash was dissolved in hydrochloric acid, with repetition of the ignition and extraction of the residue if any, and the filtrate made up to definite volume. An aliquot corresponding to 1 or 2 grams was taken for the alkalies. This was evaporated to dryness to free from the excess of acid. Clear barium hydroxide solution was added in slight excess and the solution filtered. All interfering elements are eliminated by this process, and from this point on the ordinary procedure is followed.

For lithium, caesium, and rubidium 20 grams of the dry plant were taken. This amount was carefully ashed, the ash dissolved in hydrochloric acid, and the excess of acid evaporated off. The magnesium, phosphoric acid, etc., were precipitated by lime, the lithium and sodium separated from the other alkalies by platinum-chloride, and the caesium and rubidium fractionated from the potassium in the same manner as outlined in Bulletin No. 122 of the United States Department of Agriculture. The determinations were made spectroscopically according to the method of Gooch and Phinney[1] with a Hilger wave-length spectroscope. Lithium was identified by the line 6708.2 and caesium and rubidium by the doublets 4593.3—4555.4 and 4215.6—4201.9, respectively.

[1] Am. J. Sci., 44, 392 (1892).

MANGANESE.

It was first hoped to make the manganese determination in the same subsample as that used for the determinations of barium, chromium, vanadium, and molybdenum. After the ash is fused with sodium carbonate it seems possible to precipitate the manganese with alcohol or hydrogen peroxide and determine the manganese in the insoluble portion, but while this method gives good results in many cases occasionally large errors were found. Using the Weller method the color seems to develop quicker and more uniformly when all the constituents of the plant ash are present, and the following procedure was adopted: A 2-gram sample of the well ground and mixed plant was burned, dissolved as much as possible in sulphuric acid, and a little sulphurous acid added to dissolve any manganese peroxide that may have been formed. If the concentration of acid is kept within the proper limits this method leaves nothing to be desired.

BARIUM, CHROMIUM, VANADIUM, AND MOLYBDENUM.

For this determination 20 grams of the ground plant were ashed, fused with 10 grams sodium carbonate and 0.25 gram sodium nitrate. The methods outlined by Hillebrand[1] were applied. Except when grasses (high in silica) and pine needles (high in aluminum) are to be analyzed it is necessary to evaporate the solution only to near dryness, for the normally trifling amount of silica and aluminum present will do no harm. It has been found helpful to titrate the dissolved and filtered melt nearly to the neutral point, using methyl orange as an indicator, prior to the precipitation of the mercurous salts. The results for barium and chromium were satisfactory and are believed to be reliable. The vanadium tests, however, were not so sharp cut. The color reaction with hydrogen peroxide in nitric-acid solution was used. No samples of plant ash contained enough to titrate with permanganate. It required 0.0002 gram V_2O_5 to give the characteristic vanadium test when added to 20 grams of the dry plant before incineration. The chromium and molybdenum tests were slightly more delicate. Spectroscopic tests for these elements were not used. Where vanadium, chromium, and molybdenum are reported as not found, there is less than 0.0002 gram of any one of those elements in 20 grams of the dry plant, or less than 0.001 per cent.

STRONTIUM.

The determination of strontium in plant ash is not satisfactory. A large amount of calcium is always present, a fact which necessitates a large volume in which the precipitation is to be made. It seems probable that a considerable portion of the small amount of strontium

[1] Bul. 422, U. S. Geol. Survey, pp. 138 and 150 (1910).

present escapes precipitation in both the sulphate and oxalate separations. Further, some strontium nitrate is probably dissolved by the comparatively large amount of absolute ether-alcohol which must be used to dissolve the calcium nitrate and completely wash it from the strontium nitrate. An error in the other direction arises through the difficulty of washing the strontium nitrate free from calcium salts. A spectroscopic examination of the final strontium precipitate with the Bunsen burner as a source of heat always showed the characteristic strontium line, and the calcium lines were very faint or missing. The writers believe the accuracy of the strontium determination to be such that the differences in plant composition shown in the tables for this element are not significant.

SULPHUR.

The sulphur determinations were made by two different methods, the Parr bomb method and the sodium-peroxide method. Both determinations yielded satisfactory results.

CHLORINE.

The determinations of this element were made according to Bulletin 107 (Revised) of the Bureau of Chemistry. Satisfactory results were obtained.

PHOSPHORIC ACID, CALCIUM, AND MAGNESIUM.

The phosphoric acid, calcium, and magnesium determinations were quite satisfactory, determinations by different individuals generally checking within 0.05 of 1 per cent.

MOISTURE.

The loss in weight in an electric oven kept at 105° C. was taken to represent the moisture. In some cases constant weight was reached by drying from four to six hours, but generally the drying had to run much longer. Volatile materials other than water were certainly lost, as the strong continuous odor from the samples of pine needles and onions indicated. It was not practicable to dry the onions to constant weight, and the percentages are calculated on the air-dry basis. Throughout the work duplicate determinations were made until the analyst became very familiar with the procedures, and thereafter difficult determinations were made in duplicate and unusual results were always checked up, generally by another analyst.

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